

# Isolation and characterization of wood components with aqueous acetic acid

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**Abstract:** A study was conducted on the isolation of poplar (*Populus×euramericana* (Dode) Guineir cv. I -72/58) wood components with aqueous acetic acid (AcOH) containing small amounts of sulfuric acid. The reaction time, concentration of acetic acid, ratio of liquor to wood, and concentration of acid catalyst were investigated to examine their effects on the fractionation of wood components. The three main separated components were characterized. The results showed that the optimum conditions for fractionation of poplar wood components were: 0.3% H<sub>2</sub>SO<sub>4</sub> in reaction solution, ratio of liquor to wood 6, reflux time 3 h, and 90% AcOH. The residues were mainly composed of  $\alpha$ -Cellulose and hemicellulose. The water insoluble precipitate (acetic acid lignin, AcL) had a low weight-average molecular weight range from 341 to 253 (M<sub>w</sub>) and a narrow molecular weight distribution from 1.1 to 1.2. The sugar analysis revealed the solubilized products resulted mainly from hemicellulose and exited as monosaccharides.

**Keywords:** Aqueous acetic acid; Sulfuric acid; Component separation; Poplar wood

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## Introduction

Lignocellulosic biomass is composed mainly of three chemicals of cellulose, lignin, and hemicellulose. The proportions of the three components vary with the type of biomass. Typical biomass contains 40% to 60% cellulose, 20% to 40% hemicellulose, and 10% to 25% lignin. The biomass constituents can be separated and then converted into useful chemicals. For example, cellulose is useful as the sources of various derivatives, glucose, and pulp (Sun *et al.* 2003); lignin can be used to make carbon fibers (Uraki *et al.* 1997), adhesives (Pan *et al.* 1998) and other chemicals (Kubo *et al.* 1997); and hemicellulose is the source of sugars or ethanol, and so on.

Pulping processes have previously been used to separate cellulose from lignocellulosic materials. Practically all of the production of chemical pulps in the world today is still based on the sulfite and sulfate (kraft) processes. In both processes, delignification has been achieved by introducing polar, sulphur-containing group, and thereby causing its partial degradation. The waste liquors from these processes contain the degradation products of lignin and hemicellulose, which cannot be separated in a profitable way. Additionally, the conventional pulping processes cause the severe pollution problems, which limit their developmental potential in the future. A selective and efficient separation of lignocellulose components is being made in meeting the challenges faced by the conventional pulping processes.

Increased attention has recently been paid to the use of atmosphere pulping processes with aqueous organic acid solvent as possible alternatives to the conventional pulping processes and as a method for the separation of lignocellulose components (Sano *et al.* 1989, 1990, 1995; Uraki *et al.* 1991; Pan *et al.* 1999; Dapia

*et al.* 2002). Among the various organic solvents, acetic acid is thought to be a very interesting organosolvent, owing to its ability to achieve extensive and selective delignification in a single-step operation.

In this study, poplar wood powder was refluxed in AcOH containing a small amount of acidic catalyst in order to establish satisfactory conditions for the pulping of hardwoods and fractionation of hardwood components. The physical and chemical properties of products were characterized.

## Materials and methods

Mesh wood meal (40–60) of poplar was used in this study. The sample was air-dried with a moisture content of 6.6%. Sulfuric acid and acetic acid were analytical grade reagents. N, N-dimethylformamide (DMF) was HPLC grade reagent. The composition of poplar used was 43.5% of  $\alpha$ -cellulose, 28.6% of hemicellulose, 21.3% of lignin (Klason).

## Fractionation of wood components with aqueous acetic acid

Wood meal, aqueous AcOH and sulfuric acid were mixed in a flask equipped with a condenser, and the mixture was refluxed for a preset time. After cooling, the insoluble residues (mainly cellulose) were filtered and washed with approximately 80% aqueous AcOH until the filtrate became colorless, and then washed with large quantities of distilled water. The filtrate and AcOH washings were combined and concentrated to almost dryness under reduced pressure. The water washing were poured into the concentrated solution to cause phase separation. The water insoluble precipitate (acetic acid lignin, AcL) were separated, washed with distilled water by centrifuge, and then lyophilized. The filtrate and washings were combined and concentrated under reduced pressure to obtain the solubilized products.

## Characterization of the residue, AcL and solubilized products

The contents of cellulose, klason lignin and hemicellulose in the residue were determined according to the Chinese standard (GB2677.10-81, GB2677.8-81 and GB744-89).

The molecular weight and the molecular weight distribution of the AcL were determined on a gel permeation chromatography (GPC, Shimadzu LC-10A) equipped with one GPC column

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(Shodex GPC KD-803). DMF (N, N-dimethylformamide) mixed with 0.01 M LiBr was used as the eluent at the flow rate of 1  $\text{mL}\cdot\text{min}^{-1}$ . The chromatograms were recorded with a refractometer. The molecular weights of AcL were calculated based on the molecular weight of polystyrene standard reagent.

Sugar compositions in the solubilized products were determined by a sugar analyzer on the CarboPac PA20 anion-exchange Column.

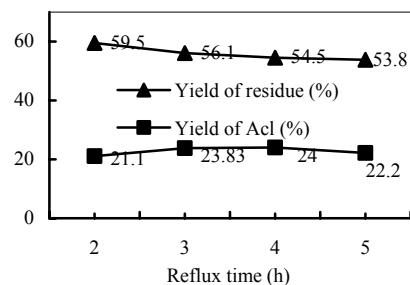
## Results and discussion

### Principle of fractionation of wood components with acetic acid

The solvent causes the dissolution of lignin and the hydrolysis of hemicellulose to sugars, leaving the cellulose in solid phase. The AcOH and the catalyst were recovered by evaporation. The concentrated solution after evaporation was poured into water for phase separation. The sugars from hemicellulose were soluble while the lignin remains in a solid phase.

### Effect of reaction conditions on the fractionation of wood components

With reflux time prolonging, the yield of residue decreased gradually and the yield of AcL increased slightly in the initial stage (Fig. 1), which indicate the progress of delignification. It is the fact that there are association forces of physical type between lignin and carbohydrates. And it is now generally accepted that chemical bonds must exist between lignin and carbohydrates. It will take some time to break these association forces and chemical bonds during the process of delignification. Therefore, enough reflux time is required for satisfactory fractionation of wood components.

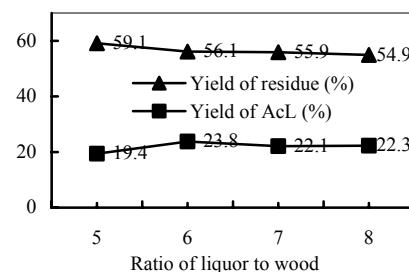


**Fig.1 Effect of reflux time on fractionation of wood component.**  
Other conditions: 0.3%  $\text{H}_2\text{SO}_4$  in reaction solution, ratio of liquor to wood 6, and 90% AcOH.

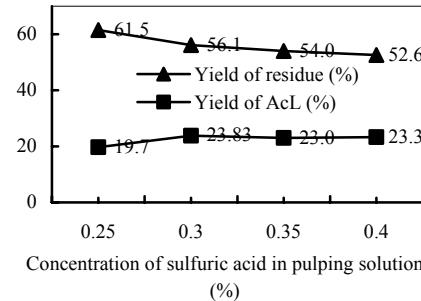
As shown in Fig. 2, the yield of residue decreased and the yield of AcL increased at the ratio of liquor to wood in the range of 5–6, which demonstrates that delignification can be promoted by increasing the ratio of liquor to wood in a certain range. With the increase of the ratio of liquor to wood (between 6 and 8), the yields of residue and AcL almost keep constant. This is because acetic acid is responsible for delignification. It is probable that the acetylation between acetic acid and lignin increases the hydrophilicity of the lignin. Thus, the solubility of the lignin in cooking liquor is increased. However, excessive acetic acid cannot lead to an obvious promotion for fractionation of wood components. Therefore, it is thought good fractionation of component might be achieved when the ratio of liquor to wood is 6.

From Fig. 3, we can see that the yield of residue decreased gradually with increase of concentration of sulfuric acid. The

yield of AcL rose at the beginning and then kept constant. The results suggest 0.3%  $\text{H}_2\text{SO}_4$  or greater is necessary to achieve good delignification. The addition of acidic catalyst can promote the delignification. However, an excessive amount of catalyst probably makes the pulping reactions more drastic, which leads to the structure damage of wood components and the unexpected degradation of cellulose.

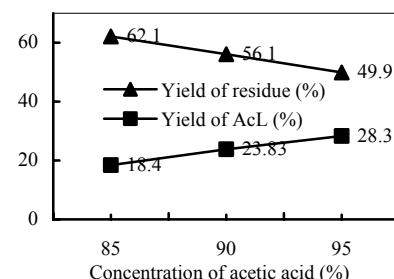


**Fig.2 Effect of ratio of liquor to wood on fractionation of wood component.** Other conditions: 0.3%  $\text{H}_2\text{SO}_4$  in reaction solution, reflux time 3 h, and 90% AcOH.



**Fig.3 Effect of concentration of sulfuric acid on fractionation of wood component.** Other conditions: reflux time 3 h, ratio of liquor to wood 6 and 90% AcOH.

With the increase of the concentration of acetic acid, the yield of the residue declined slowly and the yield of the AcL increased gradually (Fig.4). Thus, we can conclude that the increase of concentration of acetic acid is favorable to fractionation of wood component. However, 95% acetic acid may result in the extensive depolymerization of three main wood components, producing only 49.9% of residue. Therefore, 90% acetic acid might be optimum in delignification and preventing extensive and intensive damage for structures of wood components. On the other side, 90% acetic acid is superior to 95% acetic acid from the economical viewpoint.



**Fig.4 Effect of concentration of acetic acid on fractionation of wood component.** Other conditions: 0.3%  $\text{H}_2\text{SO}_4$  in reaction solution, ratio of liquor to wood 6, and reflux time 3 h.

### Characterization of three main products

Data in Table 1 show that residue 1 contains 9.2% Klason lignin, corresponding to 24.3% of the original lignin. A higher concentration of acetic acid (95%) sharply increases the removal of lignin, and slightly increases the dissolution of  $\alpha$ -Cellulose and hemicellulose. Results indicate that the selectivity of delignification is improved with the concentration of acetic acid increasing from 90% to 95%. A longer reaction time of 5 h instead of 3 h extremely increases the dissolution of lignin. As a result, lignin content of the residue goes down from 6.7% to 2.9%. At the same time, the dissolution of  $\alpha$ -Cellulose does not increase but decreases. This indicates that some side reactions may take place due to the severe pulping conditions.

**Table 1. Typical chemical composition of the residue**

Cook	Residue	Klason lignin (%)	$\alpha$ -Cellulose (%)	Hemicellulose (%)
1	1	9.2 (24.3)	54.4 (70.1)	27.4 (53.7)
2	2	6.7 (15.6)	60.5 (69.3)	28.8 (50.2)
3	3	2.9 (7.4)	58.3 (72.0)	28.4 (53.3)

**Notes:** Conditions for cook: Cook 1= 0.3%  $H_2SO_4$ , ratio of liquor to wood 6, 90% AcOH and reflux time 3 h; Cook 2=0.3%  $H_2SO_4$ , ratio of liquor to wood 6, 95% AcOH and reflux time 3 h; Cook 3= 0.3%  $H_2SO_4$ , ratio of liquor to wood 6, 90% AcOH and reflux time 5 h. The data in parentheses stand for the percentage of residual component to corresponding original one.

The AcL had a weight-average molecular weight (Mw) of 341–253 and a number-average molecular weight (Mn) of 320–221, and the polydispersity (Mw/Mn) ranged from 1.1 to 1.2 (Fig. 2). This indicates that the acid-soluble lignin has low molecular weight and a narrow molecular weight distribution. This result reveals that the substantial degradation of the macromolecular structure of lignin, such as cleavage of the ether bonds between the lignin precursors, occurs during acetic acid treatment. A higher concentration of acetic acid or a longer reaction time leads to the decrease and broad distribution of molecular weight of AcL. This indicates the severer the reaction condition, the more substantial the lignin degradation.

**Table 2. Typical molecular weight and its distribution of the AcL**

Cook*	AcL	Mw	Mn	Mw/Mn
1	1	341	320	1.1
2	2	273	234	1.2
3	3	253	221	1.2

**Note:** \*Cook: corresponding to the cook in Table 1.

It can be seen from Table 3, xylose is the predominant sugar constituent in the solubilized products, and glucose is present in smaller amounts. Arabinose, galactose and rhamnose are present as minor sugar constituents. The sugar analysis reveals the solubilized products result mainly from hemicellulose and exist as monosaccharides. This is because hemicellulose is of the amorphous state and a relatively low degree of polymerization. Moreover, most of the glycosidic linkages of hemicellulose are labile toward acid hydrolysis. When the hydrolysis has proceeded far enough, the depolymerized hemicellulose fragments are dissolved in the cooking liquor and are gradually hydrolyzed to monosaccharides (Sjöström 1993). The sugar analysis also reveals that the solubilized hemicellulose contains xylan as a major polysaccharide. A relatively high quantity of glucose indi-

cates a small amount of cellulose may be degraded under the conditions used in this study.

**Table 3. Typical composition of the solubilized products**

Cook*	Solubilized product	Arabinose (%)	Xylose (%)	Galactose (%)	Rhamnose (%)	Glucose (%)
1	1	3.2	75.5	3.6	3.9	13.9
2	2	3.9	72.7	3.4	3.4	16.6
3	3	4.0	76.8	3.5	3.6	12.2

**Note:** \*Cook: corresponding to the cook in Table 1.

### Conclusions

The experimental results revealed that all the factors, such as reaction time, concentration of acetic acid, ratio of liquor to wood, and concentration of acid catalyst, could affect the degree of delignification. The optimum conditions for fractionation of lignocellulose component were found as follows: 0.3%  $H_2SO_4$  in reaction solution, ratio of liquor to wood 6, and 90% AcOH.

Poplar wood was separated into the insoluble residues, water insoluble precipitate and dissolved sugars. The residues were mainly composed of  $\alpha$ -Cellulose and hemicellulose. The Mw and Mw/Mn of water insoluble precipitate ranged from 341 to 253, and 1.1 to 1.2, respectively. The sugar analysis revealed the solubilized products were mainly composed of predominant xylose and other monosaccharides, which were mainly from hemicellulose.

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